The Iron, Magnesium, Calcium, and Nickel Distribution in

the Murray Carbonaceous Chondrite*

KURT FREDRIKSSON (Calif. U.) 0554 02

University of California, La Jolla, California

AND

KLAUS KEIL [1962] 23 p. Double code

Space Sciences Division, National Aeronautics and Space Administration,

Ames Research Center, Moffett Field, California

Carbonaceous chondrites are of particular interest for two reasons. First, they are the only meteorites containing appreciable amounts of aqueous layer lattice silicate miner...., free sulphur, carbon, and organic material. Second, the relative abundance of elements in Type I carbonaceous chondrites is similar to that observed in the sun, indicating that these meteorites closely approach the primordial material from which the solar system was formed (Urey 1953; Mason 1960a,b, 1961; Ringwood 1961, 1962).

*This paper has first been presented at the 25th Annual Meeting of the Meteoritical Society of America, Socorro, New Mexico, September 4-5, 1962 *Submitted for Publication*
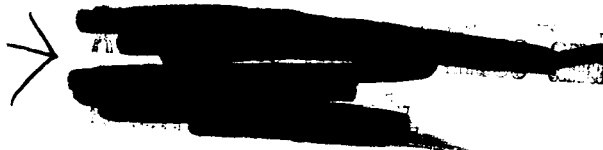
This second point, however, has later been questioned by Edwards and Urey (1955) and Urey (1961) mainly on the basis of the sodium and potassium discrepancies between carbonaceous and ordinary chondrites. Urey (1961) therefore points out that carbonaceous chondrites may have originated through transformation of high-iron group chondrites by means of "water-containing compounds." Du Fresne and Anders (1962) and Anders (1962a,b) suggested that the low-temperature layer lattice silicate matrix may have originated from the high-temperature minerals by alteration and serpentinization in situ. Ringwood (1963) assumes the carbonaceous chondrites to be by chance agglomerates of high-temperature mineral debris from enstatite and ordinary chondrites with some primitive material (for a summary see Mason 1962, 1963).

The present study has been undertaken because it seemed possible that accurate data on the composition of coexisting minerals in carbonaceous chondrites could give some clues to the problems outlined above. The results discussed below are preliminary and restricted to the Murray carbonaceous chondrite, which fell on September 20, 1950, 9 miles east of Murray, near Wildcat Creek, Kentucky (Horan 1953). However, similar studies of other types of carbonaceous chondrites are in progress.

The iron, magnesium, calcium, and nickel contents in olivine, pyroxene, and the layer lattice silicate material (Murray F of Du Fresne and Anders 1962) have been measured and the composition of some minor phases (nickel-bearing troilite, pentlandite, metallic iron) has been determined by means of electron microprobe techniques. The measurements were carried out on three carboncoated polished sections (total polished area approximately 4.5 cm^2) by use of a modified ARL electron microprobe X-ray analyzer (ARL refers to Applied Research Laboratories, Glendale, California). The

quantitative composition of the minerals mentioned was determined by using calibration curves and standards as described by Keil and Fredriksson (1963, 1964, in press). Through the courtesy of Dr. E. P. Henderson of the United States National Museum, Washington, D. C., thin sections of the Murray meteorite were made available for microscopical study.

The results of the study may be summarized as follows:

1. The composition of 63 different olivine grains and 16 different pyroxene grains has been measured by moving the samples in steps of 4 microns under the fixed electron beam, thus covering the grains with rows of analyses. Since the grains *are of similar size and* were randomly selected, it is apparent that the chondrite contains roughly four times more olivine than it does pyroxene. Zonal structure was rarely observed. However, both olivines and pyroxenes have widely varying composition. This is in agreement with the results of De Fresne and Anders (1962) and of Ringwood (1961) on some other carbonaceous chondrites. The $\frac{Fe}{Fe + Mg}$ ratios in olivine vary from 0.3 to 91.2 mol percent and in pyroxene from 0.4 to 45.4 mol percent (Tables I, II). In Figs. 1 and 2, the $\frac{Fe}{Fe + Mg}$ ratios for olivine and pyroxene, respectively, have been plotted in frequency distribution diagrams. In the diagrams this unique variability is compared to the compositional ranges of olivines and pyroxenes in LL-, L-, and H- group chondrites (Keil and Fredriksson 1964, in press). Both olivine and pyroxene show very strong maxima at low $\frac{Fe}{Fe + Mg}$ values (0 to 2 mol percent). Olivines also show a tendency of higher frequencies in the ranges observed in H-, L-, and LL- group chondrites (16 to 29 mol percent)(Keil and Fredriksson 1964, in press).

2. Small droplets (up to 20 microns) of metallic iron with varying nickel ...ents were found as inclusions in olivine grains with low $\frac{Fe}{Fe + Mg}$ ratios.

-3-

Figure 3 gives an example. The large host olivine crystal has a $\frac{Fe}{Fe + Mg}$ ratio of 0.9 mol percent and the composition of the metal is ~93% Fe and ~7% Ni. Other metal spherules (e.g., Figs. 4, 5) range in composition from 5% to 9% Ni. The nickel content of the olivine itself is less than 50 ppm.

3. The matrix of the Murray carbonaceous chondrite, which roughly amounts to 70% of the total meteorite, is composed mainly of layer lattice silicates. The composition of the matrix was ascertained by continously moving the sample 8μ/min under the electron beam and integrating the X-ray intensities every 20 seconds over areas where the main constituents (Si, Mg, Fe) varied less than ±10%. The matrix thus contains: 13 to 14% Si; ~22%Fe; 9 to 10% Mg; ~0.5% Ca; 0.5 to 1% Al; ~1 to 4% Ni; and ~1 to 4% S. The nickel sometimes appears homogeneously distributed throughout the matrix (Fig. 6); however, frequently Ni and S show a strong positive correlation (Fig. 7). This indicates that these elements in part are present in a separate mineral phase. In some cases this phase is clearly fine-grained pentlandite (Fig. 8); in many others, however, the sulfur content is too low for pentlandite. It therefore seems likely that this phase is a sulfate rather than a sulfide, impregnating the layer lattice silicate. This point of view is being supported by the fact that some of the sulfur can be leached out with distilled cold water. Furthermore, the matrix contains fine-grained inclusions of oxides and sulfides of iron (also observed by J. F. Kerridge, personal communication) less than 1 micron in diameter. While analyzing the matrix, the electron beam may occasionally have overlapped such grains, causing an increase in the iron readings. However, because of the rather constant iron values measured in the Ni and S poor areas of the layer lattice silicate material, a large contribution from these inclusions seems unlikely.

4. Small grains (up to ~100μ in diameter) of pentlandite and troilite with varying nickel contents were frequently found scattered throughout the sections. The composition of some 35 grains has been measured and was found to vary between 0.9 and 21.5 weight percent Ni. That the mineral with the higher nickel content is indeed pentlandite and not a mixture of troilite and metallic nickel-iron is demonstrated by electron beam scanning pictures in Fig. 9.

From the results presented above, certain conclusions to the origin of the Murray carbonaceous chondrite and its components may be drawn. The wide range in composition of olivines and pyroxenes in Murray and the narrow range in H-group chondrites (Figs. 1, 2) show that H-group type chondrites alone could not have been the parent rocks for Murray as was suggested by Urey (1961). The variability in composition of olivines and pyroxenes (Figs 1, 2) also indicates that these minerals could not have been formed in a one-event process from one source, but must have originated in different environments and from various sources. After formation they were apparently mixed together mechanically. Similar conclusions have recently been derived by Ringwood (1963) who assumes the carbonaceous chondrites to be chance agglomerates of some primitive layer lattice silicates with debris from enstatite and ordinary chondrites. However, the results of the present study show that this rather complex model is still too simplified, since one cannot account for the majority of olivines and pyroxenes observed in Murray by assuming enstatite and ordinary chondrites to be the only sources (cf. Figs. 1, 2). Enstatite chondrites contain almost exclusively pyroxene with less than 0.3 percent divalent iron, while ordinary chondrites contain olivines and pyroxenes with $\frac{Fe}{Fe + Mg}$ ratios varying in narrow ranges as indicated in Figs. 1 and 2.

It is readily seen that it is difficult to account for the olivine with $\frac{Fe}{Fe + Mg}$ ratios up to some 15 and above 30 mol percent, as well as for pyroxene of 0.5 to 12 and above 27 mol percent, which make up the majority of high-temperature silicates observed in Murray. Silicates with similar iron contents have only very rarely been observed in noncarbonaceous chondrites, for example, in the achondrite Kapoeta (Fredirksson and Keil 1963) and in polymineralic inclusions in the Odessa iron meteorite (Marshall and Keil 1964, in preparation).

In addition there is an apparent difference in the calcium contents of olivines and pyroxenes in ordinary chondrites in comparison to the ones observed in the Murray carbonaceous chondrite. The calcium content in olivines of both L- and H- group chondrites is below 0.05% (Keil and Fredriksson 1964, in press), while the Murray olivines on the average contain about 0.2%. The L- and H- group pyroxenes, on the other hand, contain on the average 0.47% Ca, while the Murray pyroxenes contain about 0.7% with individual crystals frequently showing more than 1.0%. This again makes it difficult to understand the olivines and pyroxenes in the Murray carbonaceous chondrite to be debris from common chondrites.

The proposition that the Murray carbonaceous chondrite is a mechanical mixture of minerals from various sources is further indicated by the droplets of metallic iron included in some FeO-poor olivines (Figs. 3, 4, 5). The origin of these inclusions may be ascribed to reduction of divalent nickel and iron of the olivine to metal by heating the olivine above the melting point of iron under slightly reducing conditions as has been shown experimentally by A. Henriques (personal communication) and K. Fredriksson (unpublished).

The heating and reduction had to occur before agglomeration of the various minerals, since the Murray carbonaceous chondrite as a whole has apparently not been heated above 250°C for a reasonable length of time (Du Fresne and Anders 1962).

The question of the origin of the layer lattice silicate matrix is of importance to any hypothesis on the origin of the carbonaceous chondrites. The high iron and nickel contents of the matrix and the low iron and nickel contents of most olivines indicate that the main mass of the matrix material did not originate through alteration (serpentinization) of the high-temperature minerals in situ. These results contradict the conclusions drawn by Du Fresne and Anders (1962), but generally seem to support Ringwood's (1963) and Fredriksson's (1963) conclusions.

The results of the study may be summarized as follows: The Murray carbonaceous chondrite is a mechanical mixture of minerals formed under different conditions at different localities. Most of the olivines and pyroxenes observed cannot represent debris of common chondrite types as suggested by Ringwood (1963) because their compositions differ markedly (Figs. 1, 2). The main mass of the layer lattice silicate matrix apparently is not an in situ alteration product of the associated olivines and pyroxenes.

ACKNOWLEDGMENTS

REFERENCES

Urey, H. C. 1954, "Discussion," Nuclear Processes in Geologic Settings, N.R.C. Pub. 400, Washington, D. C., 49.

Mason, B. 1960a, "Origin of Chondrules and Chondritic Meteorites," Nature 186, 230-231.

_____ 1960b, "The Origin of Meteorites," J. Geophys. Res. 65, 2965-2970.

_____ 1961, "Reply to Dr. Harold C. Urey's Criticism of the Paper by Brian Mason, 'The Origin of Meteorites,'" ibid. 66, 3979-3980.

Ringwood, A. E. 1961, "Chemical and Genetic Relationships Among Meteorites," Geochim. et Cosmochim. Acta 24, 159-197.

_____ 1962, "Present Status of the Chondritic Earth Model," Researches on Meteorites (John Wiley and Sons, Inc., New York), 198-216.

Edwards, G., and Urey, H. C. 1955, "Determination of Alkali Metals in Meteorites by a Distillation Process," Geochim. et Cosmochim. Acta 7, 154-168.

Urey, H. C. 1961, "Criticism of Dr. B. Mason's Paper on 'The Origin of Meteorites,'" J. Geophys. Res. 66, 1988-1991.

Du Fresne, E. R., and Anders, E. 1962, "On the Chemical Evolution of the Carbonaceous Chondrites," Geochim. et Cosmochim. Acta 26, 1085-1114.

Anders, E. 1962a, "On the Origin of Carbonaceous Chondrites," Preprint, EFINS 62-27.

_____ 1962b, "Meteorities and the Early History of the Solar System," ibid., 62-50.

Ringwood, A. E. 1963, "The Origin of High Temperature Minerals in Carbonaceous

Chondrites," J. Geophys. Res. 68, 1141-1143.

Mason, B. 1962-1963, "The Carbonaceous Chondrites," Space Sci. Rev. 1,

621-646.

Horan, J. R. 1953, "The Murray, Calloway County, Kentucky, Aerolite,"

Meteoritics 1, 114-121.

Keil, K., and Fredriksson, K. 1963, "Electron Microprobe Analysis of Some

Rare Minerals in the Norton County Achondrite," Geochim. et Cosmochim. Acta

27, 939-947.

_____ . 1964, in press, "The Iron, Magnesium, and

Calcium Distribution in Coexisting Olivines and Rhombic Pyroxenes of Chondrites,"

J. Geophys. Res.

Fredriksson, K., and Keil, K. 1963, "The Light-Dark Structure in the Pantar and

Kapoeta Stone Meteorites," Geochim. et Cosmochim. Acta 27, 717-739.

Marshall, R. R., and Keil, K. 1964, in preparation, "Inclusions in the Odessa

Iron Meteorite Showing Effects of Primordial Differentiation, Icarus.

Fredriksson, K. 1963, "Chondrules and the Meteorite Parent Bodies," Trans.

New York Acad. Sci., Ser. II, 25, 756-769.

TABLE I.- CARBONACEOUS CHONDRITE MURRAY. COMPOSITION OF 63
INDIVIDUAL OLIVINE CRYSTALS FROM 3 POLISHED SECTIONS.

Crystal no.	Weight percent			Mol percent $\dfrac{Fe}{Fe + Mg}$
	Fe	Mg	Ca	
1	0.2	34.1	0.41	0.3
2	.3	33.7	.40	.4
3	.3	33.7	.32	.4
4	.3	33.8	.51	.4
5	.3	33.8	.42	.4
6	.3	33.8	.49	.4
7	.4	33.1	.32	.5
8	.4	33.6	n.d.	.5
9	.4	33.7	.15	.5
10	.4	33.8	.32	.5
11	.4	34.0	.18	.5
12	.5	33.5	n.d.	.6
13	.5	33.5	.15	.6
14	.5	33.5	.17	.6
15	.6	32.8	.33	.8
16	.6	33.8	n.d.	.8
17	.7	32.7	n.d.	.9
18	.7	33.1	.22	.9
19	.7	33.5	<.1	.9
20	.7	33.5	.19	.9
21	.7	33.8	.14	.9

TABLE I.- CARBONACEOUS CHONDRITE MURRAY. COMPOSITION OF 63 INDIVIDUAL

OLIVINE CRYSTALS FROM 3 POLISHED SECTIONS - Continued

Crystal no.	Weight percent			Mol percent $\dfrac{Fe}{Fe + Mg}$
	Fe	Mg	Ca	
22	0.8	32.7	0.16	1.1
23	.8	34.0	n.d.	1.0
24	.9	33.4	.13	1.2
25	.9	33.4	.18	1.2
26	1.0	32.9	.14	1.3
27	1.1	33.7	n.d.	1.4
28	1.1	33.7	n.d.	1.4
29	1.3	31.3	.21	1.8
30	1.5	32.5	.19	2.0
31	2.2	31.9	.10	2.9
32	2.2	32.3	.16	2.9
33	2.2	33.0	<.1	2.8
34	2.9	31.4	.10	3.9
35	3.3	31.6	.11	4.4
36	5.2	31.4	n.d.	6.7
37	7.1	30.2	n.d.	9.3
38	7.6	27.9	.17	10.6
39	8.3	28.9	.46	11.1
40	10.0-11.6	28.0-27.3	.10	13.5-15.6
41	15.3	25.5	.17	20.7
42	15.3	25.6	.10	20.6

TABLE I.- CARBONACEOUS CHONDRITE MURRAY. COMPOSITION OF 63 INDIVIDUAL OLIVINE CRYSTALS FROM 3 POLISHED SECTIONS - Concluded

Crystal no.	Weight percent			Mol percent $\dfrac{Fe}{Fe + Mg}$
	Fe	Mg	Ca	
43	15.3	25.9	0.12	20.5
44	15.5	25.5	.12	20.9
45	15.8	25.6	<.1	21.2
46	16.5	24.9	.12	22.4
47	16.6	24.3	.17	22.9
48	17.7	24.2	<.1	24.2
49	18.5	23.4	.21	25.6
50	18.6	23.6	.21	25.5
51	19.8	22.8	<.1	27.4
52	19.8	22.9	.11	27.4
53	19.9	22.7	.12	27.7
54	20.1	22.9	.21	27.6
55	22.1	21.4	.16	31.0
56	23.6	19.7	.31	34.3
57	24.0	20.2	.31	34.1
58	27.4	18.4	<.1	39.3
59	30.6	15.4	.18	46.4
60	35.8	11.9	.19	56.7
61	45.4	3.7	.20	84.2
62	49.8	2.6	.12	89.3
63	52.6	2.2	.18	91.2

TABLE II.- CARBONACEOUS CHONDRITE MURRAY. COMPOSITION OF 16 INDIVIDUAL
PYROXENE CRYSTALS FROM 3 POLISHED SECTIONS.

Grain no.	Weight percent			Mol percent $\dfrac{Fe}{Fe + Mg}$
	Fe	Mg	Ca	
1	0.2	23.5	0.32	0.4
2	.5	23.2	.31	.9
3	.5	23.4	.26	.9
4	.7	22.2	1.4	1.4
5	.7	23.6	1.1	1.3
6	.9	23.9	.74	1.6
7	1.2	22.3	1.1	2.3
8	1.6	22.1	1.1	3.1
9	2.5	21.6	1.2	4.8
10	3.3	21.4	.78	6.3
11	5.3	20.4	.61	10.2
12	10.4	18.4	<.1	19.7
13	14.2	15.5	.15	28.5
14	15.7	14.6	.24	31.9
15	17.4	13.1	.46	36.6
16	25.4	13.3	.76	45.4

FIGURE CAPTIONS

Fig. 1.- Frequency distribution of the mol-percent ratios $\frac{Fe}{Fe + Mg}$ in 63 individual olivine crystals. Part B gives the values between 0 to 8 mol percent on a larger scale.

Fig. 2.- Frequency distribution of the mol-percent ratios $\frac{Fe}{Fe + Mg}$ in 16 individual pyroxene crystals.

Fig. 3.- Euhedral olivine crystal containing droplet of metallic nickel-iron (high reflecting). Matrix is layer lattice silicate. Dark stripes on olivine are remainders from carbon coating. Reflected light.

Fig. 4.- Olivine chondrule (round) and olivine grain containing droplets of nickel-iron (high reflecting). Matrix is layer lattice silicate material. Reflected light.

Fig. 5.- Olivine chondrule (round) and olivine grain containing droplets of nickel-iron (black) clearly inside the olivine. Matrix is layer lattice silicate material. Same area as in Fig. 4, but polarized reflected light.

Fig. 6.- Pictures obtained with a scanning electron beam. Association of olivine with low- (right side) and high- (left side) iron contents in a layer lattice silicate matrix (center). BSE = backscattered electron image; Fe, Ni, Mg, Si = pictures giving the distribution of these elements in the scanned area. The Fe image illustrates the high-iron content in the matrix and the different iron contents in the two olivines. The nickel seems homogenously distributed throughout this part of the matrix (Ni image). The Mg image illustrates the high magnesium content in the iron-poor olivine.

Fig. 7.- Positive correlation between Ni, S, and to a less extent, Fe, in the matrix material of the Murray carbonaceous chondrite. The sample was moved 8μ/min, while the counts were integrated every 20 seconds.

Fig. 8.- Pictures obtained with a scanning electron beam. Association of olivines, layer lattice silicate matrix, and fine-grained pentlandite in the matrix. BSE = backscattered electron image; Mg, Si, Fe, Ni, S = pictures showing the distribution of these elements in the scanned area. The pentlandite shows up in the BSE as well as in the Fe, Ni, and S images. Parts of the layer lattice silicates show high Ni values with only moderate S values.

Fig. 9.- Pictures obtained with a scanning electron beam. Association of pentlandite embedded in layer lattice silicate matrix. BSE = backscattered electron image; Fe, S, Ni = pictures showing the distribution of these elements in the scanned area. In the BSE the pentlandite with high-average atomic number appears bright. The Fe_{K_α} image shows similar amounts of Fe in both pentlandite and surrounding silicate matrix. The K_α pictures of S and Ni show the homogeneous distribution of these elements in the pentlandite.

A

NUMBER OF CASES

AVERAGES AND RANGES IN
COMPOSITION OF OLIVINES
IN LL-, L-, AND H-GROUP CHON-
DRITES (ACCORDING TO KEIL &
FREDRIKSSON[17])

H   L LL

RATIOS $\dfrac{Fe}{Fe + Mg}$ IN MOL PERCENT

B

NUMBER OF CASES

RATIOS $\dfrac{Fe}{Fe + Mg}$ IN MOL PERCENT

Figure 1.

AVERAGES AND RANGES IN COMPOSITION
OF RHOMBIC PYROXENES IN LL-, L-, AND H-GROUP
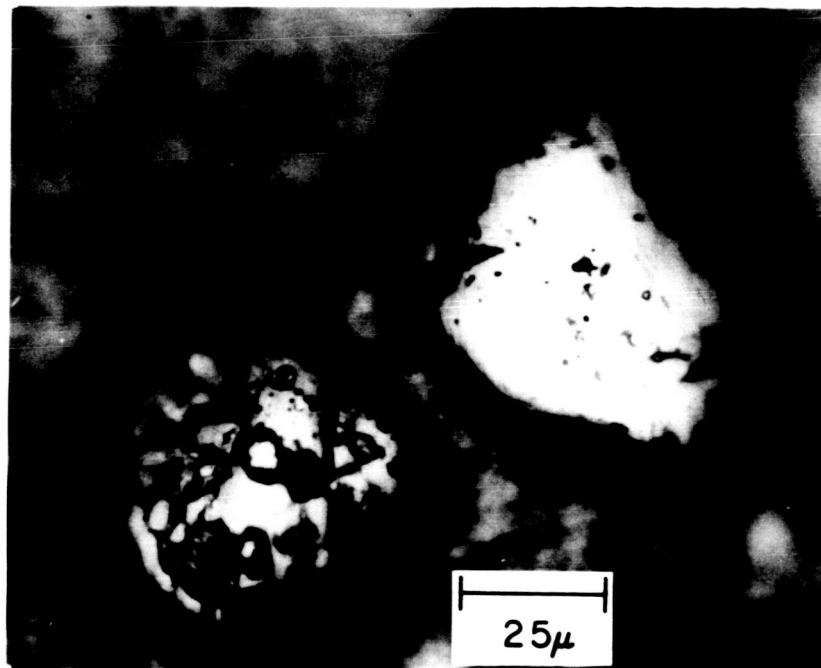CHONDRITES (ACCORDING TO KEIL & FREDRIKSSON[17])
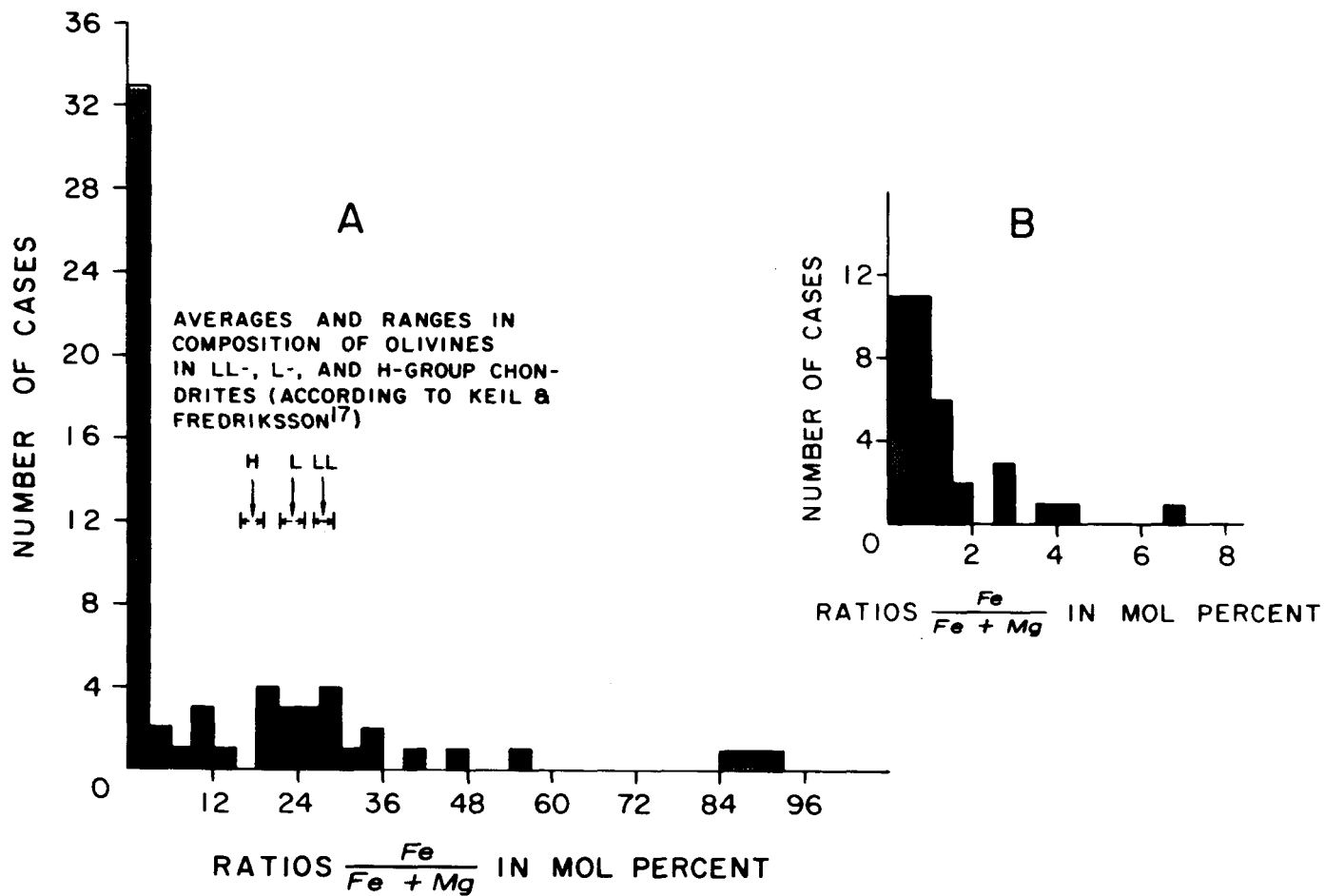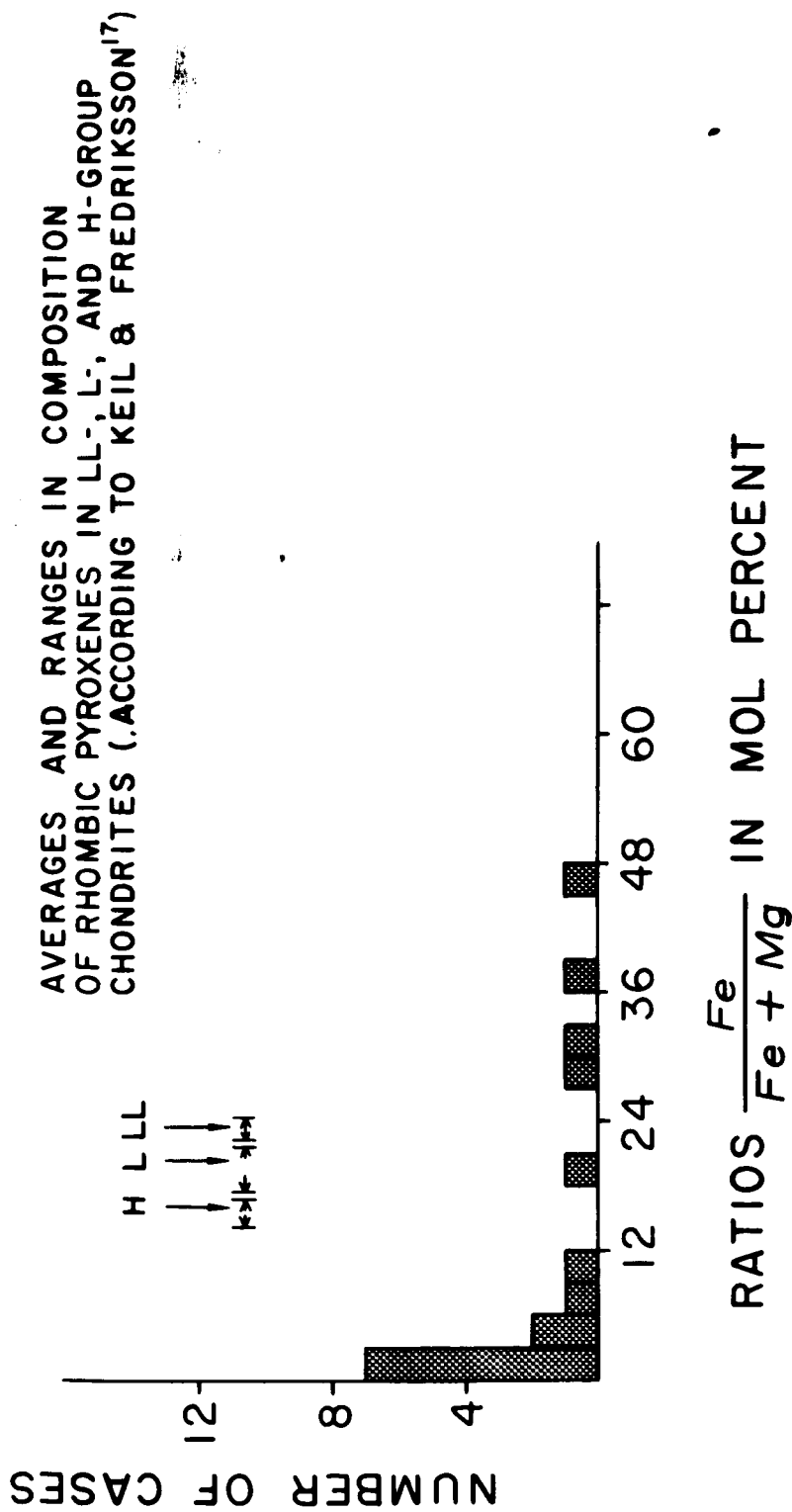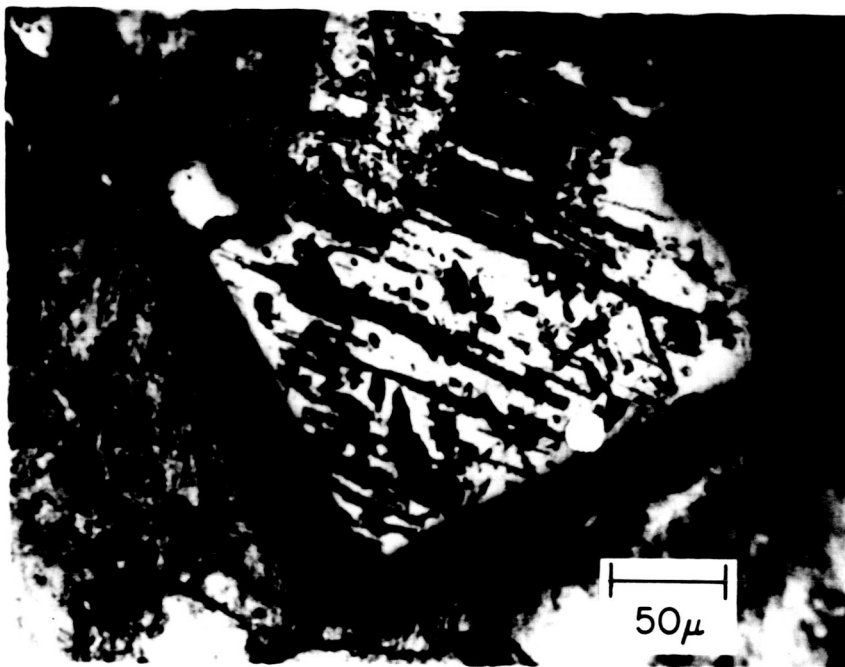
Figure 2.

Figure 3.

Figure 4.
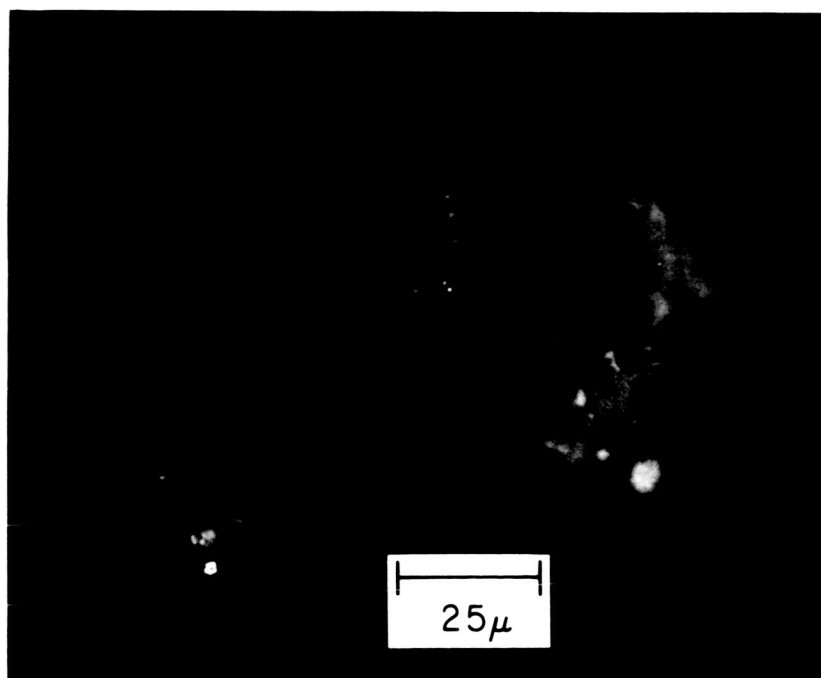
Figure 5.

BSE   Fe   Ni
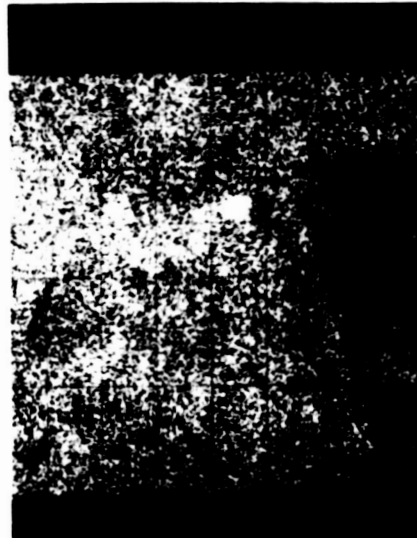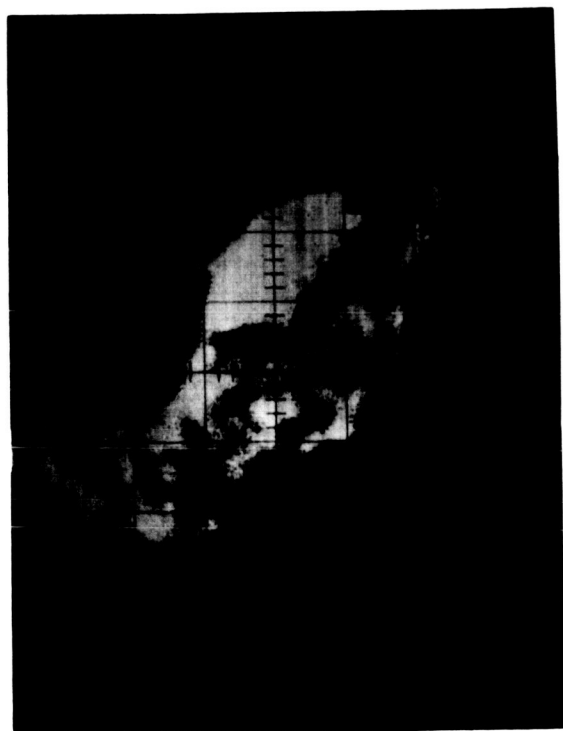
Mg   Si

|—— 50μ ——|
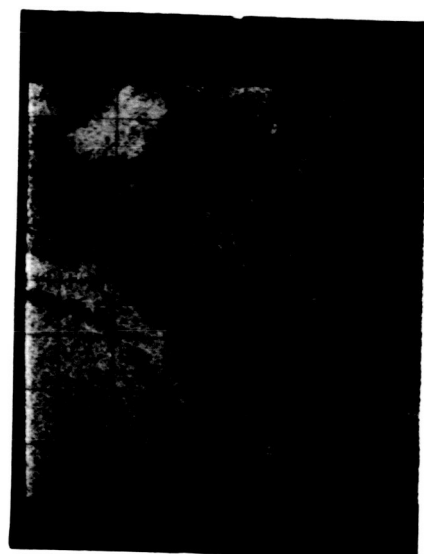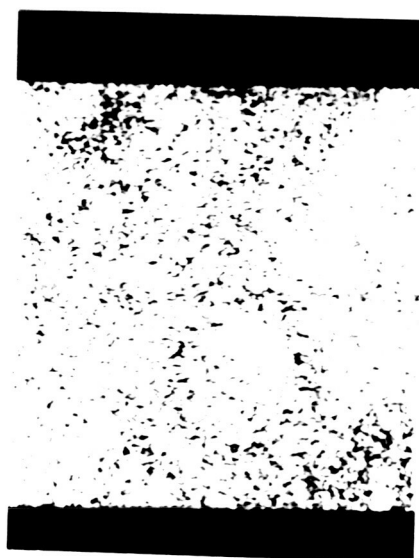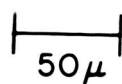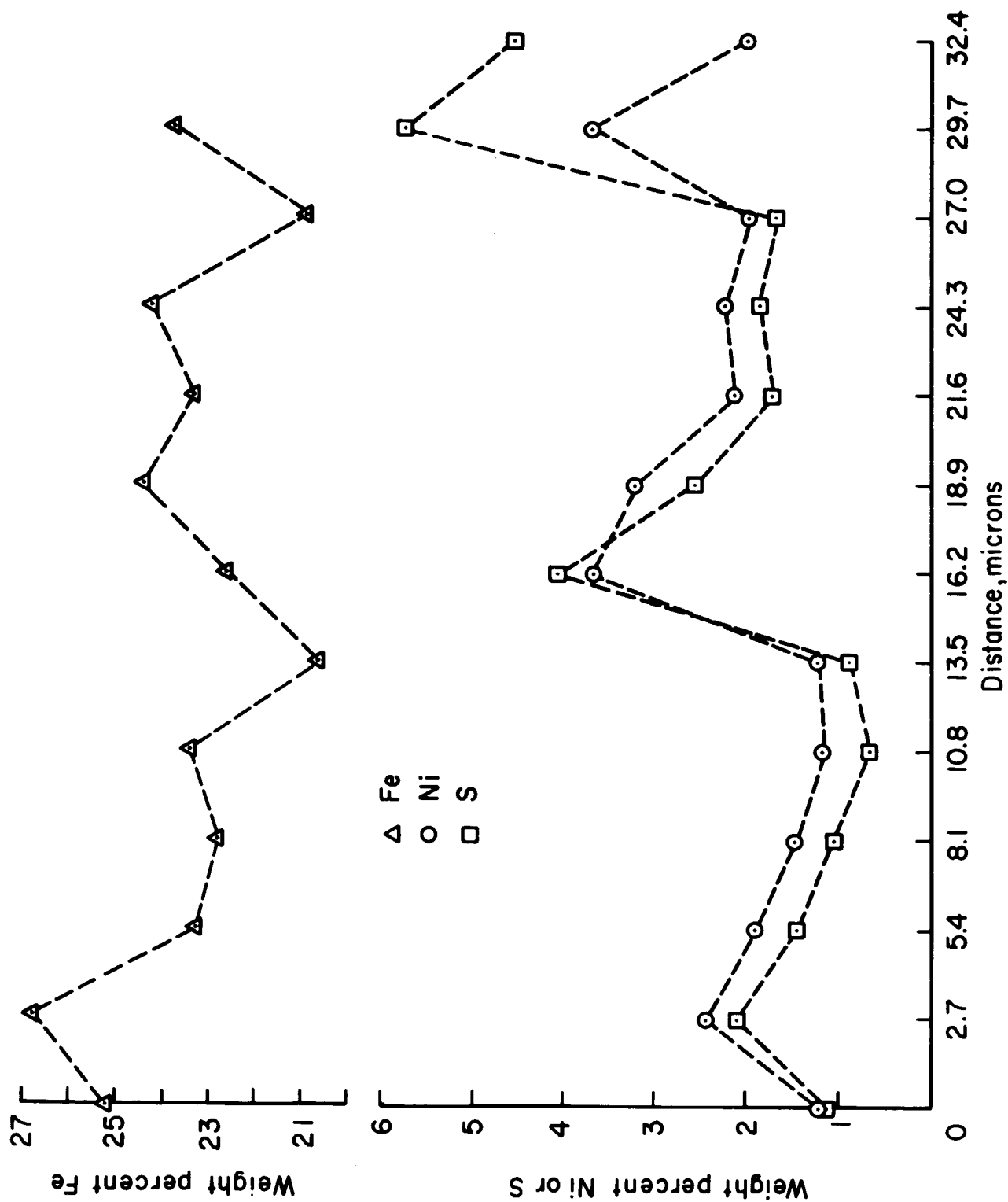
Figure 6.

Figure 7.

BSE

Mg

Si

Fe

Ni

S

50μ

Figure 8.

Fe

S

BSE

Ni

50 μ

Figure 9.